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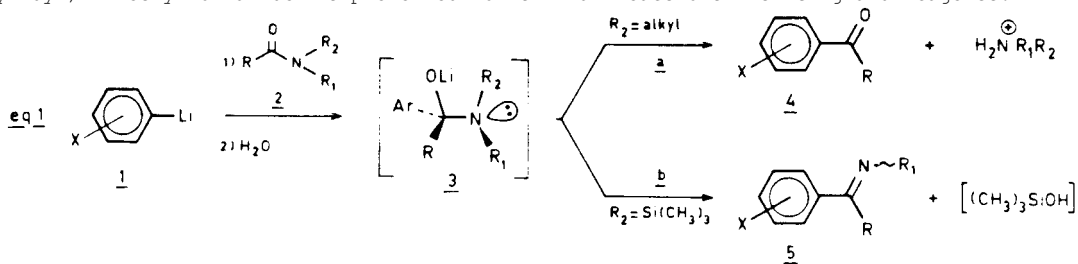
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SYNTHESIS OF ARYLIMINES FROM N-SILYLAMIDES AND ARYL LITHIUM COMPOUNDS

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**Abstract:** Various arylimines were synthesized by the addition of N-silylated-N-alkyl- or N-aryl-amides to aryllithium compounds.

The addition reaction of organolithium compounds 1 to the carbonyl group of N,N-disubstituted amides 2 is well known to yield carbonyl compounds 4 (eq. 1a).<sup>1,2</sup> This reaction is particularly valuable in the synthesis of aldehydes from DMF<sup>1,2</sup> or N-methylformanilide<sup>3</sup> whereas N-(2-pyridyl)-N-methylformamide<sup>4</sup> is preferred for similar reactions with Grignard reagents.

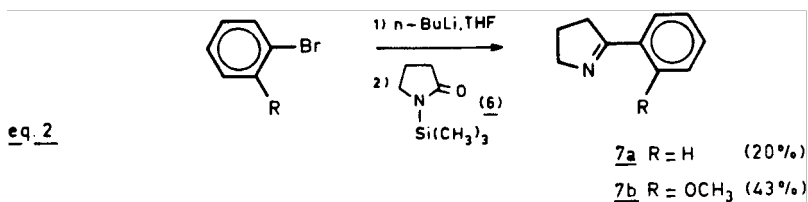


(X = H, CH<sub>3</sub>, OCH<sub>3</sub>; R = H, alkyl, aryl; R<sub>1</sub> = alkyl, aryl)

In connection with synthetic studies using N-silylated-amides<sup>5</sup> 2 ( $\text{R}_2 = \text{Si}(\text{CH}_3)_3$  and N-silylated-lactams<sup>5</sup> we have found that aryllithium compounds 1 readily react with amides 2 to give imines<sup>6</sup> 5 instead of carbonyl compounds 4 (eq. 1b).

Treatment of a solution of phenyllithium in THF at -78°C with N-methyl-N-trimethylsilyl propionamide, either neat or as a solution in THF, and subsequent warming to room temperature gave after a standard work-up, N-methyl-ethylphenylimine in 73% yield. The results of the conversion of aryllithium compounds with several N-silylated amides are summarized in Table I. The imineformation is strongly dependant on the basicity of the lithium reagent as alkyllithium compounds only yielded products derived from deprotonation of the N-silylated acetamides. Isomerically pure imines were obtained from all formamides (entries 6, 10, 11) and N-methyl-N-trimethylsilylacetamides (entries 3, 7). The stereochemical assignment is based on comparison of <sup>1</sup>H-NMR data with those published. For the acetophenone- and 2-acetylfuran-imines (entries 3, 7), the E-configuration was established on basis of the observed coupling constants in the <sup>1</sup>H-NMR spectra ( $J_{\text{H,H}} < 1.0 \text{ Hz}$  for  $\text{HC}=\text{N}-\text{CH}$ ).<sup>7</sup>

The imines 5 can be reduced in situ to amines [71%, (NaBH<sub>4</sub>, CH<sub>3</sub>OH); 75%, 83% and 60%, (LiAlH<sub>4</sub>, THF) for entries 1, 2, 3 and 4 respectively] or hydrolysed to aldehydes or ketones (e.g. entry 1, 80% phenylethylketone).



The present method also allows preparation of aryl-Δ<sup>1</sup>-pyrrolines 7 from N-silylated-pyrrolidone 6, although yields are low so far. Thus reaction of phenyllithium with 6 gave 20% of 7 after chromatography (identical with an independently prepared sample<sup>8</sup>) (eq. 2).

**Table I** Synthesis of Arylimines

	Aryl-	R	R <sub>1</sub>	yield(%) <sup>a</sup>	Z/E <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	73	30/70
2	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	60	40/60
3	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	63	0/100
4	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	77	—
5	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	80	—
6	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	55	0/100
7	C <sub>4</sub> H <sub>3</sub> O	CH <sub>3</sub>	CH <sub>3</sub>	57	0/100
8	C <sub>4</sub> H <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	55	40/60
9	C <sub>4</sub> H <sub>3</sub> O	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	79	45/55
10	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	35	0/100
11	(o-OCH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	70	0/100

a. Isolated yield by distillation; b. Z/E ratio determined by NMR.

The elucidation of the stereochemical features of this new imine formation and the use of functionalized organolithium reagents is presently under investigation.

#### References

1. B.J. Wakefield in "Comprehensive Organometallic Chemistry", G. Wilkinson, F.G.A. Stone and E.W. Abel, eds., Pergamon, Oxford, 1982, vol. 7, chapter 44.
2. B.J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon: Oxford, 1974.
3. N.S. Narasimhan and R.S. Mali, Tetrahedron, 1975, 31, 1005,
4. D. Comins and A.I. Meyers, Synthesis, 1978, 403; and references cited therein.
5. a) I. Fleming in "Comprehensive Organic Chemistry", D. Barton, and W.D. Ollis, eds., Pergamon, Oxford, 1979, chapter 13; b) E. Colvin, "Silicon in Organic Synthesis", Butterworths, London, 1981, chapter 19.
6. G. Tennant in "Comprehensive Organic Chemistry", D. Barton and W.D. Ollis, eds., Pergamon, Oxford, 1979, chapter 8.
7. H. Ahlbrecht, S. Fischer, Tetrahedron, 1970, 26, 2837.
8. W. Koller and P. Schlack, Chem. Ber. 1963, 96, 93.

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